

[54] METHOD FOR FABRICATING CERAMIC FILAMENTS AND HIGH DENSITY TAPE CASTING METHOD

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[58] Field of Search 156/89, 181, 167, 242, 156/243, 245, 246, 244.11, 244.24, 250; 264/60, 63, 67, 114, 118, 121, 125, 311; 429/40, 45, 247; 425/75, 73, 425, 435

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[57] ABSTRACT

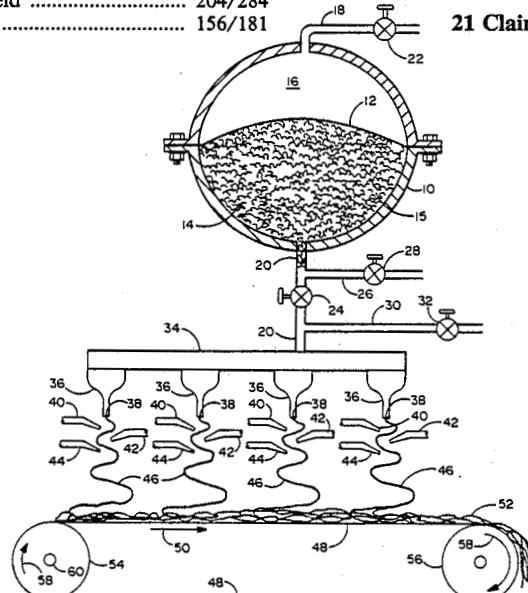
An apparatus and method is disclosed for fabricating mats of ceramic material comprising preparing a slurry of ceramic particles in a binder/solvent, charging the slurry into a vessel, forcing the slurry from the vessel into spinneret nozzles, discharging the slurry from the nozzles into the path of air jets to enhance the sinuous character of the slurry exudate and to dry it, collecting the filaments on a moving belt so that the filaments overlap each other thereby forming a mat, curing the binder therein, compressing and sintering the mat to form a sintered mat, and crushing the sintered mat to produce filament shaped fragments.

A process is also disclosed for producing a tape of densely packed, bonded ceramic particles comprising forming a slurry of ceramic particles and a binder/solvent, applying the slurry to a rotating internal molding surface, applying a large centrifugal force to the slurry to compress it and force excess binder/solvent from the particles, evaporating solvent and curing the binder thereby forming layers of bonded ceramic particles and cured binder, and separating the binder layer from the layer of particles.

Multilayers of ceramic particles are cast in an analogous manner on top of previously formed layers. When all of the desired layers have been cast the tape is fired to produce a sintered tape.

For example, a three-layer tape is produced having outer layers of highly compressed filament shaped fragments of strontium doped lanthanum ("LSM") particles and a center layer of yttria stabilized zirconia ("YSZ") particles.

21 Claims, 3 Drawing Sheets



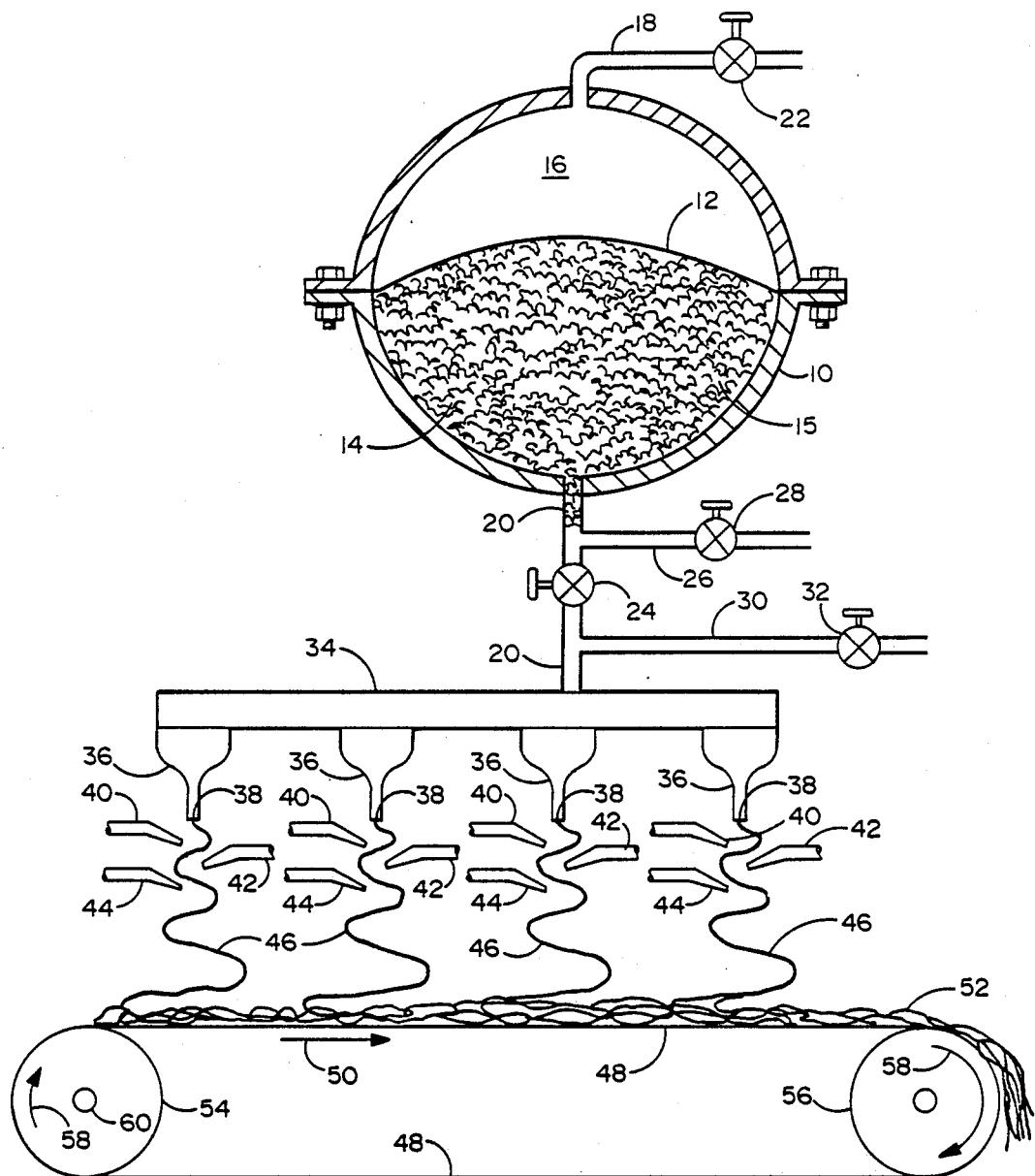


FIG. 1

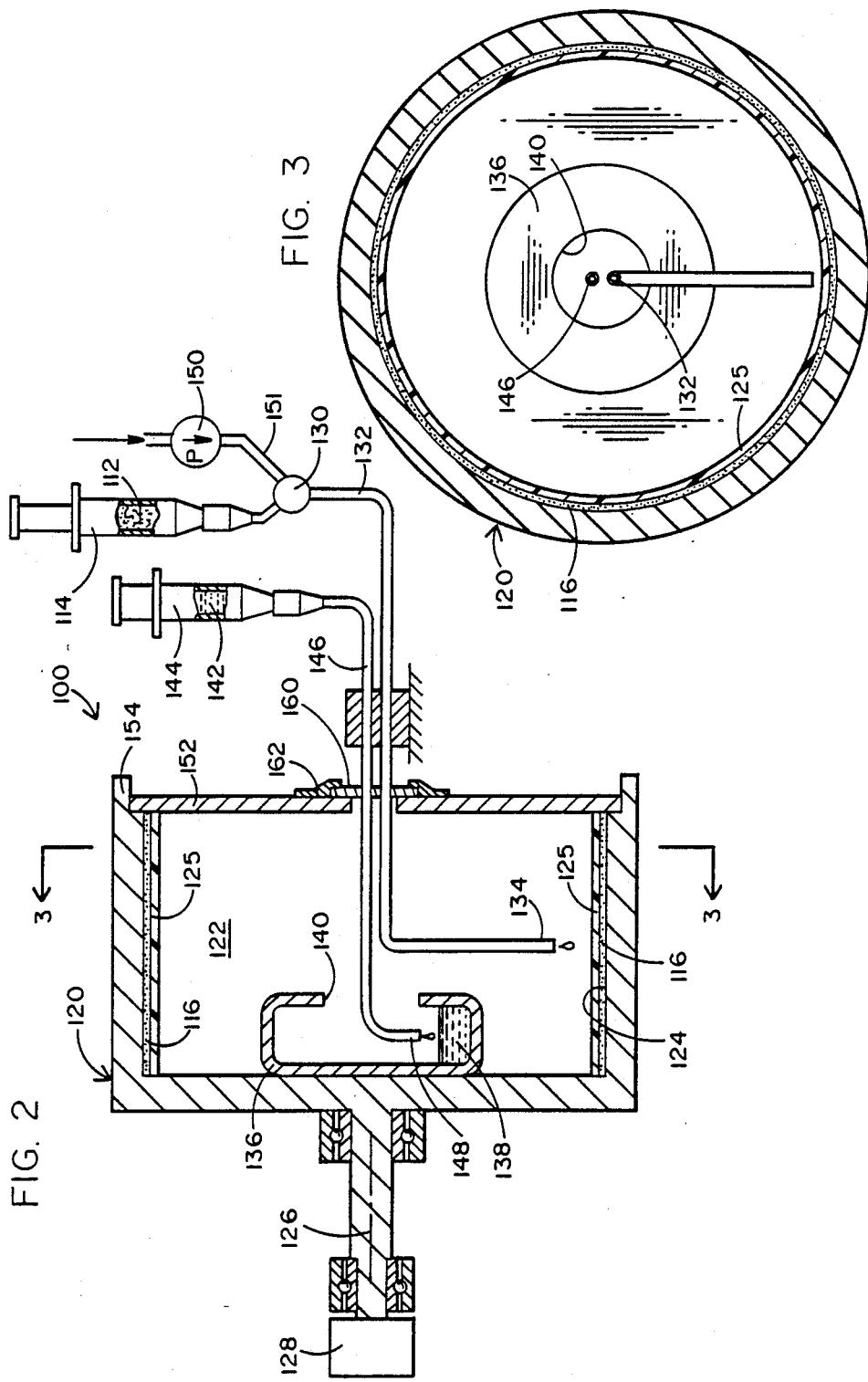


FIG. 4

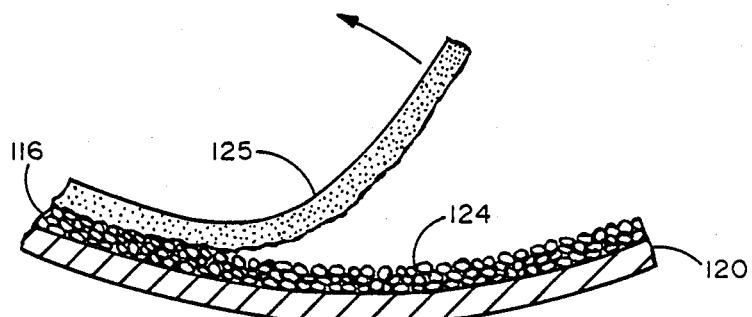


FIG. 5

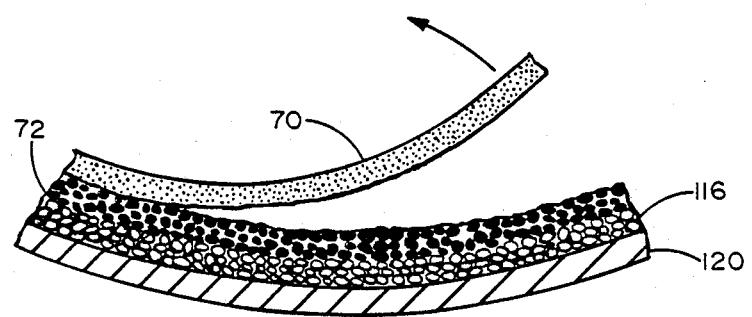
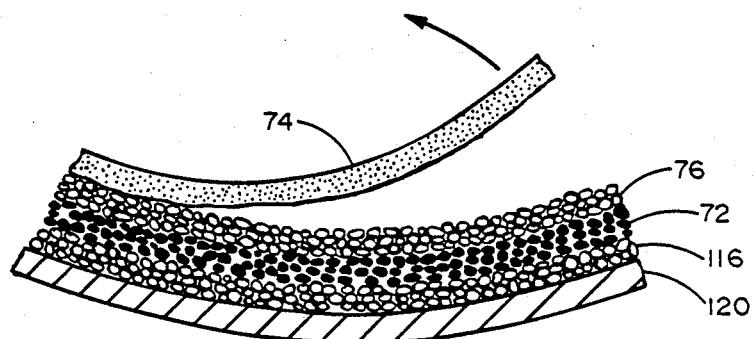


FIG. 6



**METHOD FOR FABRICATING CERAMIC  
FILAMENTS AND HIGH DENSITY TAPE  
CASTING METHOD**

**ORIGIN OF INVENTION**

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the Contractor has elected to retain title.

**BACKGROUND OF THE INVENTION**

This invention is related to my copending Ser. No. 921,574, filed Oct. 21, 1986, now U.S. Pat. No. 4,839,121, entitled improved High Density Tape Casting System which is hereby incorporated herein by reference.

In the process for the electrolytic separation of oxygen from air, using solid electrolyte membranes such as zirconia, porous electrodes are needed. At present, ceramic electrode material is supplied as a fine powder and it is highly desirable to increase the particle size to increase the porosity of the electrode. However, as the particle size increases, contact area between particles decreases thereby increasing the electrode electrical resistance, an undesirable occurrence. An improved porous electrode configuration is therefore needed having interconnecting pores and large contact area between the particles of the electrode material. Such improved porous electrodes can then be used in thin ceramic membrane, commonly called tapes.

Thin ceramic membranes or tapes are typically made from ground ceramic suspended in a mixture of solvents, binders, and other components, to form a slurry which is spread on a flat surface and allowed to cure by air-drying. The flexible, pliable tape is then fired in a kiln to remove solvents and other impurities, and results in a hard ceramic substrate for use in capacitors. Tapes are also formed in multilayer ceramic sandwiches comprising electrodes and insulators for separation of oxygen from air, and for use as the membrane of high temperature solid electrolyte fuel cells and high temperature solid electrolyte electrolysis cells and the like, hereinafter referred to collectively as "tape-containing devices".

Strontium doped lanthanum magnaite, which for brevity is sometimes referred to herein as "LSM", is known to be a good material for use in electrodes produced by tape casting methods. LSM having the mole ratio  $La_{0.8}Sr_{0.2}MnO_3$  is available as a submicron size material having a surface area of 3 to 5  $m^2/g$  from HUA Associates, Rolla, Mo.

Eight mole percent yttria stabilized zirconia, which for brevity is sometimes referred to herein as "YSZ", is known to be a good material for use in the electrolyte layer in such tape-containing devices.

**SUMMARY OF THE INVENTION**

There is provided by the principles of this invention a method of forming a mat of overlying sinuous filaments having a predetermined thickness comprising blending a mixture comprising finely divided solid particles a binder operable for bonding the solid particles together, and a solvent for the binder, into an uniformly dispersed slurry; transforming the slurry into a plurality of downwardly falling filaments; deflecting the plurality of downwardly falling filaments with a plurality of impinging gas streams operative for deflecting and

bending the filaments into a plurality of downwardly falling sinuous filaments while simultaneously removing the solvent therefrom by evaporation; and collecting the plurality of sinuous filaments on a moving surface in such a manner that the plurality of sinuous filaments overlap each other in a predetermined amount thereby forming a mat of overlying sinuous filaments having a predetermined thickness. In another embodiment of this invention the method further comprises compressing the thusly produced mat to increase the filament-to-filament contact therein thereby producing a pressed mat; heating the pressed mat to a temperature operable for increasing the amount of filament-to-filament bonding therein thereby producing a bonded mat; and comminuting the bonded mat thereby producing filament shaped fragments of bonded agglomerates of the solid particles. In yet a further embodiment the produced filament shaped fragments are ceramic.

There is also provided by the principles of this invention a method of producing filament shaped fragments of bonded agglomerates of strontium lanthanum manganite particles comprising blending a mixture comprising finely divided solid particles of strontium lanthanum manganite, a binder operable for bonding the solid particles together, and a solvent for the binder, into an uniformly dispersed slurry; transforming the slurry into a plurality of downwardly falling filaments; deflecting and drying the plurality of downwardly falling filaments with a plurality of impinging gas streams operative for deflecting and bending the filaments into a plurality of downwardly falling sinuous filaments while simultaneously removing the solvent therefrom by evaporation; collecting the plurality of sinuous filaments on a moving surface in such a manner that the plurality of sinuous filaments overlap each other in a predetermined amount thereby forming a mat of overlying sinuous filaments having a predetermined thickness; compressing the mat to increase the filament-to-filament contact therein thereby producing a pressed mat; sintering the pressed mat at a temperature operable for increasing the amount of filament-to-filament bonding therein thereby providing a bonded mat; and comminuting the bonded mat thereby producing filament shaped fragments of bonded agglomerates of strontium lanthanum manganite particles. In a further embodiment the binder is polyvinyl butyral and the solvent is methylene chloride. In another embodiment the filament shaped fragments have an average length of at least about 0.003 inches and a width of at least about 0.00025 inches.

There is also provided by the principles of this invention a method of producing a tape of densely packed, bonded solid particles comprising blending a mixture comprising finely divided solid particles, a binder operable upon curing for bonding the finely divided solid particles together, and a solvent for the binder, into an uniformly dispersed slurry; introducing the thusly blended uniformly dispersed slurry onto a rotating internal molding surface; and applying an effective centrifugal force to the slurry thusly introduced onto the rotating internal molding surface which is operable for transforming the slurry into an outer, densely packed, annular layer of the solid particles coated with a small amount of the solvent and the binder which is compressed against the molding surface by the centrifugal force and an inner annular layer of the solvent and the binder which is compressed against the outer, densely packed, annular layer of the solid particles by the cen-

trifugal force, the amount of binder used for forming the uniformly dispersed slurry being in excess of an amount required to bond the solid particles together. After forming the outer and inner annular layers and while applying the centrifugal force, the method further comprises removing the solvent from the outer and inner annular layers by evaporation; allowing the binder coating the solid particles in the outer annular layer to bond the solid particles together thereby forming an outer, densely packed, bonded, annular layer of the solid particles, and allowing the binder in the inner annular layer to cure into a solid state thereby forming an inner annular layer of cured binder; removing the applied centrifugal force from the outer and inner annular layer and thereafter separating the inner annular layer of cured binder from the outer, densely packed, bonded, annular layer of the solid particles; and separating the outer densely packed, bonded, annular layer of the solid particles from the molding surface thereby producing a tape of densely packed, bonded solid particles. In one embodiment the finely divided solid particles used to produce the tape of densely packed, bonded solid particles are strontium lanthanum manganite particles. In one embodiment the binder is polyvinyl butyral and the solvent is methylene chloride. In one embodiment the effective centrifugal force is at least about 1800 g and preferably at least about 2000 g. In another embodiment the method further comprises sintering the thusly produced tape of sensely packed, bonded solid particles to produce a tape of sensely packed, sintered solid particles.

There is also provided byd the principles of this invention a method of producing a multilayer tape of sensely packed, bonded solid particles comprising:

(a) blending a first mixture comprising finely divided first solid particles having a chemical composition, a first binder operable upon curing for bonding the finely divided first solid particles together, and a first solvent for the first binder, into an uniformly dispersed first slurry;

(b) introducing the thusly blended uniformly dispersed first slurry onto a rotating internal molding surface;

(c) applying an effective centrifugal force to the first slurry thusly introduced onto the rotating internal molding surface which is operable for transforming the first slurry into an outer, densely packed, annular layer of the first solid particles coated with a small amount of the first solvent and the first binder which is compressed against the molding surface by the centrifugal force, and an inner annular layer of the first solvent and the first binder which is compressed against the outer, densely packed, annular layer of the first solid particles by the centrifugal force, the amount of the first binder used for forming the uniformly dispersed first slurry in step (a) being in exvcess of an amount required to bond the first solid particles together;

(d) after forming the outer and inner layers and while applying the centrifugal force, removing the first solvent from the outer and inner annular layers by evapo- 60

ration;

(e) allowing the first binder coating the first solid particles in the outer, densely packed, annular layer to bond the first solid particles together thereby forming an outer densely packed, bonded, annular layer of the first solid particles, and allowing the first binder in the inner annular layer to cure into a solid state thereby forming an inner annular layer of cured first binder;

5 (f) removing the applied centrifugal force from the outer and inner annular layers and thereafter separating the inner annular layer of cured first binder from the outer, densely packed, bonded annular layer of the first solid particles;

10 (g) blending a second mixture comprising finely divided second solid particles having a chemical composition which is the same or different from the chemical composition of the first solid particles, a second binder operable upon curing for bonding the finely divided second solid particles together, and a second solvent for the second binder, into an uniformly dispersed second slurry, the second binder and the second solvent not being capable of chemically attacking the first binder in he thusly produced outer, densely packed, bonded, annular layer of the first solid particles;

15 (h) rotating the internal molding surface containing the outer, densely packed, bonded, annular layer of the first solid particles;

(i) introducing the thusly blended uniformly dispersed second slurry onto the rotating outer, densely packed, bonded, annular layer of the first solid particles;

20 (j) applying an effective centrifugal force to the second slurry thusly introduced onto the rotating outer, densely packed, bonded, annular layer of the first solid particles which is operable for transforming the second slurry into a second, densely packed, annular layer of the second solid particles coated with a small amount of the second solvent and the second binder which is compressed against the outer, densely packed, bonded, annular layer of the first solid particles by the last mentioned centrifugal force, and an inner annular layer of the second solvent and the second binder which is compressed against the second, densely packed, annular layer of the second solid particles by the last mentioned centrifugal force, the amount of the second binder used for forming the uniformly dispersed second slurry in step (g) being in excess of an amount required to bond the second solid particles together;

25 (k) after forming the second, densely packed, annular layer of the second solid particles and the inner annular layer of the second solvent and the second binder, removing the second solvent therefrom by evaporation; and

30 (l) allowing the second binder coating the second solid particles in the second, densely packed, annular layer of the second solid particles to bond the second solid particles thereof together thereby forming a second, densely packed, bonded, annular layer of the second solid particles, and allowing the second binder in the last mentioned inner annular layer to cure into a solid state thereby forming an inner annular layer of cured second binder.

35 In one embodiment the method of this invention further comprises after step (l) removing the last mentioned applied centrifugal force from the annular layers and thereafter separating the inner annular layer of cured second binder from the second, densely packed, bonded, annular layer of the second solid particles thereby forming a composite layer structure which comprises the outer, densely packed, bonded, annular layer of the first solid particles and bonded thereto the second, densely packed, bonded annular layer of the second solid particles; and separating the composite layer structure from the internal moldiang surface thereby producing a multilayer tape of densely packed, bonded solid particles. In yet another embodiment the chemical composition of the finely divided first saolid

particles is strontium lanthanum manganite, and the chemical composition of the finely divided second solid particles is yttria stabilized zirconia.

In one embodiment the method of this invention further comprises after step (1) removing the last mentioned applied centrifugal force from the annular layers and thereafter separating the inner annular layer of cured second binder from the second, densely packed, bonded, annular layer of the second solid particles; blending a third mixture comprising finely divided third solid particles having a chemical composition which is the same or different from the chemical composition of the second solid particles, a third binder operable for bonding the finely divided third solid particles together, and a third solvent for the third binder, into an uniformly dispersed third slurry, the third binder and the third solvent not being capable of chemically attacking the second binder in the thusly formed second,

the finely divided first and third solid particles is strontium lanthanum manganite, and the chemical composition of the finely divided second solid particles is yttria stabilized zirconia. In another embodiment the first and third binder is polyvinyl butyral, the second binder is linseed oil, the first and third solvent is methylene chloride, and the second solvent is petroleum spirits.

There is also provided by the principles of this invention an apparatus for forming a mat of overlying sinuous filaments which comprise solid particles, the apparatus comprising a manifold; means in fluid communication with the manifold for feeding a viscous slurry which comprises finely divided solid particles, a binder operable for bonding the solid particles together, and a solvent for the binder, into the manifold; a plurality of orifices in fluid communication with the manifold, each of the orifices having a downwardly facing outlet operable for producing, when the apparatus is in use, a downwardly directed fluid filament of such viscous

solvent, introducing the thusly formed slurry into one zone of a vessel having two zones separated by a diaphragm. Pressurizing the other zone of the vessel thereby displacing the diaphragm into the first zone containing the slurry and forcing the slurry through a series of fine spinneret nozzles into the path of alternately-pulsed airjets, thereby deflecting the slurry exudates rapidly back and forth and thereby forming partially dried sinuous filaments which are accumulated onto a moving surfacing in such a manner that the sinuous filaments overlap and form a mat. In a further embodiment the mat is pressed to increase filament-to-filament contact, then heated to form a bonded mat and then comminuted to produce filament shaped fragments of bonded agglomerates of the solid ceramic particles. These bonded agglomerate fragments have high porosity and relative low electrical resistance and can be used as the ceramic material in formulating a slurry for tape casting.

It has been discovered that if an excess of binder and solvent are used in formulating the slurry for tape cast-

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic of my apparatus for forming and collecting overlapping sinuous filaments on a moving surface.

FIG. 2 is an apparatus useful for conducting my method of forming a high density single layer or multi-layer tapes.

FIG. 3 is a view taken along line 1—3 of FIG. 2.

FIG. 4 is a cross-sectional view, greatly enlarged, of a cured high density single layer tape with the cured excess binder layer being removed.

FIG. 5 is a cross-sectional view similar to FIG. 4 of a two layer tape with the cured excess binder of the second ceramic layer being removed.

FIG. 6 is a cross-sectional view similar to FIG. 5 of a three layer tape with the cured excess binder of the third ceramic layer being removed.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

A slurry is formed from commercially available LSM

vessel from its source thereby charging zone 14 with slurry 15. As slurry 15 flows into vessel 10, diaphragm 12 is displaced upwards. When a sufficient amount of slurry is introduced into the vessel valve 28 is closed.

Conduit 30 is connected to a source of solvent (not shown) and valve 32 is opened while valve 24 remains closed and solvent is pumped through conduits 30 and 20 into the manifold and nozzles 36 and discharged through outlets 38 thereby flushing and cleaning out the apparatus of any residue that might be left over from its last use and displacing air from inside the manifold and spinneret nozzles with solvent vapors. Thereafter valve 32 is closed and pressurized gas from a source (not shown) is connected to conduit 18 and valve 22 opened thereby pressurizing upper zone 16 in vessel 10.

Pressurized gas in upper zone 16 exerts a downward force on diaphragm 12. When valve 24 is opened, the slurry in zone 16 is forced through conduit 20 by the gas

—source is zone 16 into manifold 24 spinneret nozzle

erates of the solid metal oxide or ceramic particles, for example filament shaped fragments of LSM having a diameter of about 0.00025 inches and average length of about 0.003 inches. Other diameters and lengths of filament shaped fragments can be produced if desired including mixtures to produce a predetermined size distribution. For example in an alternative embodiment of this invention, the diameters of orifices 38 are not all the same so that a predetermined mix of filament diameters are produced.

The thusly produced filament shaped fragments of bonded agglomerates of metal oxide or ceramic particles can be used to produce a ceramic tape in all types of tape casting machines. However, another embodiment of this invention uses the filament shaped fragments to produce a high density tape in the apparatus shown in FIGS. 2 and 3 which is more fully explained in my copending application previously identified.

The high density tape casting system 100 shown in

11

is rotated rapidly to create high centrifugal forces thereby compressing the slurry against the molding surface. The higher density particles in the slurry are compressed with greater force against molding surface 124 than the binder/solvent thereby producing a very high compacted density of particles in the cast tape and forcing the excess binder and solvent out of and abutted against the layer of densely packed ceramic particles thereby forming, after curing, inner layer 125 of cured binder adjacent to compacted solid particle layer 116.

The slurry 112 includes ceramic particles, or preferably filament shaped fragments of agglomerates thereof, a binder in excess of the amount necessary to bind the particles together, and a solvent for the binder in an amount effective for dispersing the ceramic particles in the slurry uniformly over the molding surface. the solvent also has sufficiently high vapor pressure that it can be removed by evaporation.

12

After the binder has cured plates 152, 160 and 162 are removed from housing member 154 and inner annular layer 125 of cured solid binder is peeled off of outer annular layer 116 of bonded solid particles in the manner shown in FIG. 4.

If only a single layer of bonded solid particles is required then layer 116 is removed from molding surface 124 and further processed to produce a sintered tape. However in one embodiment of this invention layer 116 is not removed from molding surface 124 and a second slurry of solid or ceramic particles is cast directly on top of layer 116 using its inner cylindrical surface as a molding surface for the second slurry in a process exactly analogous to the method used for forming the first layer of solid particles as will be explained.

Since the first layer has not at this point been sintered it still contains binder which can be chemically attacked by the solvent in the second slurry. For this reason it is important to select as a second binder/solvent system

is applied to the exposed inner surface of layer 72 in a manner analogous to the application of the first two slurries into the chamber. As in the formation of the first two layers the applied centrifugal force forms a thirds densely packed layer of solid particles with excess binder/solvent forming a fourth layer abutted thereto. Solvent is evaporated in an analogous manner as that described earlier and the binder in the third and fourth layers allowed to cure. After the binder has cured outer layer 74 of binder is peeled off of third later 76 of bonded cured densely packed third solid particles as shown in FIG. 6.

The composite tape structure comprising layers 116, 72 and 76 can be removed from molding surface 124 and fired to produce a three layer sintered ceramic. Alternatively additional layers of solid particles can be added in an analogous manner to form as many layers as desired.

Tape structures can be folded or laminated to other green tape structures and fired to produce unlimited variety of multilayered ceramic tapes for various uses. However the binder/solvent system used for forming a particular layer of solid particles must be non-deleteriously reactive with the cured binder in the immediately preceding layer of solid particles in order to prevent alteration thereof. Therefore binder/solvent systems which will dissolve or penetrate into the cured binder of the previous layer should not be used. Binder/solvent systems which are immiscible with the binder used in the previous layer are therefore preferred. Binders which crosslink during curing usually are not deleteriously attached by binder/solvents in the subsequently cast slurry and therefore are also preferred.

In casting a sandwich membrane tape for the electrolytic separation of oxygen from air, three layers are needed: a central layer of YSZ particles, between two layers of LSM particles. The latter serves as the conducting electrode layer. Thus, the layer deposited and first compacted in FIG. 4 would be an LSM layer.

FIG. 5, the second slurry would be YSZ slurry which has been poured in place, compressed against the LSM layer, cured, and is having its excess binder peeled away. As in all subsequently applied slurries, this second slurry should have its liquid components chosen so as not to deleteriously attack the cured binder of the first layer such as a solvent which cannot dissolve the first binder, or alternatively by use of a binder in the LSM layer which undergoes polymerization during cure.

FIG. 6 is a third layer has been cast and cured which in this example is a second LSM layer. Again, the liquid components of the LSM slurry are chosen not to dissolve the cured binder of the YSZ layer. Since only the previous layer is likely to be affected, the solvent/binder mixtures can be an alternating pair of mixtures, regardless of how many layers are cast.

To enhance ease of handling, and to provide easier removal from the molding surface or drum, a protective coating layer can be deposited on the drum before slurry casting, and then cured. Such a protective layer can also be applied after casting is complete, to completely cover the tape. With proper choice of components, the cast solids will not penetrate into this first coat, which will define a sharp interface between it and the first layer. Finally, the multilayer tape is removed from the casting drum, and kiln fired, in the usual manner. This removes all organics and impurities, leaving only the ceramics, sintered into a strong assembly. By control of the centrifugal forces, solvents, and binders

involved, control may be had over density, interpenetration, and strength, in any desired combination of qualities.

While the preferred embodiments of the present invention have been described, it should be understood that various changes, adaptations and modifications may be made thereto without departing from the spirit of the invention and the scope of the appended claims. It should be understood, therefore, that the invention is not to be limited to minor details of the illustrated invention shown in the figures and that variations in such minor details will be apparent to one skilled in the art.

Therefore it is understood that the present disclosure and embodiment of this invention described herein are for purposes of illustration and example and that modifications and improvements may be made thereto without departing from the spirit of the invention or from the scope of the claims. The claims, therefore, are to be accorded a range of equivalents commensurate in scope with the advances made over the art.

What is claimed is:

1. A method of forming a mat of overlying sinuous filaments having a predetermined thickness comprising:

- (a) blending a mixture comprising
  - (i) finely divided solid particles,
  - (ii) a binder operable for bonding said solid particles together, and
  - (iii) a solvent for said binder, into an uniformly dispersed slurry;
- (b) transforming said slurry into a plurality of downwardly falling filaments;
- (c) deflecting said plurality of downwardly falling filaments with a plurality of impinging gas streams operative for deflecting and bending said filaments into a plurality of downwardly falling sinuous filaments while simultaneously removing said solvent therefrom by evaporation; and
- (d) collecting said plurality of sinuous filaments on a moving surface in such a manner that said plurality of sinuous filaments overlap each other a predetermined amount thereby forming a mat of overlying sinuous filaments having a predetermined thickness.

2. The method of claim 1, further comprising compressing said thusly produced mat to increase the filament-to-filament contact therein thereby producing a pressed mat;

heating said pressed mat to a temperature operable for increasing the amount of filament-to-filament bonding therein thereby producing a bonded mat; and

commuting said bonded mat thereby producing filament shaped fragments of bonded agglomerates of said solid particles.

3. The method of claim 2, wherein said produced filament shaped fragments are ceramic.

4. The method of claim 1, wherein said transforming of said slurry into a plurality of downwardly falling filaments includes extruding the slurry.

5. A method of producing filament shaped fragments of bonded agglomerates of strontium lanthanum manganese particles comprising:

- (a) blending a mixture comprising
  - (i) finely divided solid particles of strontium lanthanum manganite,
  - (ii) a binder operable for bonding said solid particles together, and

- (iii) a solvent for said binder, into an uniformly dispersed slurry;
- (b) transforming said slurry into a plurality of downwardly falling filaments;
- (c) deflecting and drying said plurality of downwardly falling filaments with a plurality of impinging gas streams operative for deflecting and bending said filaments into a plurality of downwardly falling sinuous filaments while simultaneously removing said solvent therefrom by evaporation;
- (d) collecting said plurality of sinuous filaments on a moving surface in such a manner that said plurality of sinuous filaments overlap each other a predetermined amount thereby forming a mat of overlying sinuous filaments having a predetermine thickness;
- (e) compressing said mat to increase the filament-to-filament contact therein thereby producing a pressed mat;
- (f) sintering sand pressed mat at a temperature operable for increasing the amount of filament-to-filament bonding therein thereby providing a bonded mat; and
- (g) comminuting said bonded mat thereby producing filament shaped fragments of bonded agglomerates of strontium lanthanum manganite particles.

6. The method of claim 5, wherein said filament shaped fragments have a length of at least about 0.003 inches and a width of at least about 0.00025 inches.

7. The method of claim 5, wherein said binder is polyvinyl butyral and said solvent is methylene chloride.

8. The method of claim 5, wherein said transforming of said slurry into a plurality of downwardly falling filaments includes extruding the slurry.

9. A method of producing a tape of densely packed, bonded solid particles comprising:

- (a) blending a mixture comprising
  - (i) finely divided solid particles,
  - (ii) a binder operable upon curing for bonding said finely divided solid particles together, and
  - (iii) a solvent for said binder, into a uniformly dispersed slurry;
- (b) introducing said thusly blended uniformly dispersed slurry onto a rotating internal molding surface;
- (c) applying an effective centrifugal force to said slurry thusly introduced onto said rotating internal molding surface which is operable for transforming said slurry into an outer, densely packed, annular layer of said solid particles coated with a small amount of said solvent and said binder which is compressed against said molding surface by said centrifugal force and an inner annular layer of said solvent and said binder which is compressed against said outer, densely packed, annular layer of said solid particles by said centrifugal force, the amount of binder used for forming said uniformly dispersed slurry in step (a) being in excess of an amount required to bond said solid particles together;
- (d) after forming said outer and inner annular layers and while applying said centrifugal force, removing said solvent from said outer and inner annular layers by evaporation;
- (e) allowing said binder coating said solid particles in said outer annular layer to bond said solid particles together thereby forming an outer, densely packed, bonded, annular layer of said solid particles, and

allowing said binder in said inner annular layer to cure into a solid state thereby forming an inner annular layer of cured binder;

- (f) removing said applied centrifugal force from said outer and inner annular layer and thereafter separating said inner annular layer of cured binder from said outer, densely packed, bonded, annular layer of said solid particles; and
- (g) separating said outer densely packed, bonded, annular layer of said solid particles from said molding surface thereby producing a tape of densely packed, bonded solid particles.

10. The method of claim 9, wherein said effective centrifugal force is at least about 1800 g.

11. The method of claim 9, further comprising sintering said thusly produced tape of sensely packed, bonded solid particles to produce a tape of sensely packed, sintered solid particles.

12. The method of claim 9, wherein said finely divided solid particles used to produce said tape of densely packed, bonded solid particles are strontium lanthanum manganite particles.

13. The method of claim 9, wherein said binder is polyvinyl butyral and said solvent is methylene chloride.

14. A mehtod of producing a multilayer tape of sensely packed, bonded solid particles comprising:

- (a) blending a first mixture comprising
  - (i) finely divided first solid particles having a chemical composition,
  - (ii) a first binder operable upon curing for bonding said finely divided first solid particles together, and
  - (ii) a first solvent for said first binder, into an uniformly dispersed first slurry;
- (b) introducing said thusly blended uniformly dispersed first slurry onto a rotating internal molding surface;
- (c) applying an effective centrifugal force to said first slurry thusly introduced onto said rotating internal molding surface which is operable for transforming said first slurry into an outer, densely packed, annular layer of said, first solid particles coated with a small amount of said first solvent and said first binder which is compressed against said molding surface by said centrifugal force, and an inner annular layer of said first solvent and said first binder which is compressed against said outer, densely packed, annular layer of said first solid particles by said centrifugal force, the amount of said first binder used for forming said uniformly dispersed first slurry in step (a) being in excess of an amount required to bond said first solid particles together;
- (d) aftr forming said outer and inner layers and while applying said centrifugal force, removing said first solvent from said outer and inner annular layers by evaporation;
- (e) allowing said first binder coating said first solid particles in said outer, densely packed, annular layer to bond said first solid particles together thereby forming an outer densely packed, bonded, annular layer of said first solid particles, and allowing said first binder in said inner annular layer to cure into a solid state thereby forming an inner annular layer of cured first binder;
- (f) removing said applied centrifugal force from said outer and inner annular layers and thereafter separating said inner annular layer of cured first binder

from said outer, densely packed, bonded annular layer of said first solid particles;

(g) blending a second mixture comprising

- (i) finely divided second solid particles having a chemical composition which is different from said chemical composition of said first solid particles, 5
- (ii) a second binder operable upon curing for bonding said finely divided second solid particles together, and
- (ii) a second solvent for said second binder, into an uniformly dispersed second slurry, said second binder and said second solvent not being capable of chemically attacking said first binder in said thusly produced outer, densely packed, bonded, annular layer of said first solid particles; 15

(h) rotating said internal molding surface containing said outer, densely packed, bonded, annular layer of said first solid particles;

(i) introducing said thusly blended uniformly dispersed second slurry onto said rotating outer, densely packed, bonded, annular layer of said first solid particles; 20

(j) applying an effective centrifugal force to said second slurry thusly introduced onto said rotating outer, densely packed, bonded, annular layer of said first solid particles which is operable for transforming said second slurry into a second, densely packed, annular layer of said second solid particles 25

coated with a small amount of said second solvent and said second binder which is compressed against said outer, densely packed, bonded, annular layer of said first solid particles by said last mentioned centrifugal force, and an inner annular layer 30

of said second solvent and said second binder which is compressed against said second, densely packed, annular layer of said second solid particles by said last mentioned centrifugal force, the amount of said second binder used for forming said 35

uniformly dispersed second slurry in step (g) being in excess of an amount required to bond said second solid particles together;

(k) after forming said second, densely packed, annular layer of said second solid particles and said inner 40

annular layer of said second solvent and said second binder, removing said second solvent therefrom by evaporation;

(l) allowing said second binder coating said second solid particles in said second, densely packed, annular layer of said second solid particles to bond said second solid particles thereof together thereby forming a second, densely packed, bonded, annular layer of said second solid particles, and allowing said second binder in said last mentioned inner 45

annular layer to cure into a solid state thereby forming an inner annular layer of cured second binder; 50

(m) removing said last mentioned applied centrifugal force from said annular layers and thereafter separating said inner annular layer of cured second binder from said second, densely packed, bonded, annular layer of said second solid particles thereby forming a composite layer of said second solid particles thereby forming a composite layer of said second solid particles which comprises said outer, densely packed, bonded, annular layer of said first solid particles and bonded thereto said second, densely packed, 55

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bonded annular layer of said second solid particles; and

(n) separating said composite layer structure from said internal molding surface thereby producing a multilayer tape of densely packed, bonded solid particles.

15. The method of claim 14, wherein said chemical composition of said finely divided first solid particles is strontium lanthanum manganite, and said chemical composition of said finely divided second solid particles in yttria stabilized zirconia.

16. A method of producing a multilayer tape of densely packed, bonded solid particles comprising:

- (a) blending a first mixture comprising
- (i) finely divided first solid particles having a chemical composition,
- (ii) a first binder operable upon curing for bonding said finely divided first solid particles together, and
- (ii) a first solvent for said first binder, into an uniformly dispersed first slurry;

(b) introducing said thusly blended uniformly dispersed first slurry onto a rotating internal molding surface;

(c) applying an effective centrifugal force to said first slurry thusly introduced onto said rotating internal molding surface which is operable for transforming said first slurry into an outer, densely packed, annular layer of said first solid particles coated with a small amount of said first solvent and said first binder which is compressed against said molding surface bby said centrifugal force, and an inner annular layer of said first solvent and said first binder which is compressed against said outer, densely packed, annular layer of said first solid particles by said centrifugal force, the amount of said first binder used for forming said uniformly dispersed first slurry in step (a) being in excess of an amount required to bond said first solid particles together;

(d) after forming said outer and inner layers and while applying said centrifugal force, removing said first solvent from said outer and inner annular layers by evaporation;

(e) allowing said first binder coating said first solid particles in said outer, densely packed, annular layer to bond said first solid particles together thereby forming an outer densely packed, bonded, annular layer of said first solid particles, and allowing said first binder in said inner annular layer to cure into a solid state thereby forming an inner annular layer of cured first binder;

(f) removing said applied centrifugal force from said outer and inner annular layers and thereafter separating said inner annular layer of cured first binder from said outer, densely packed, bonded annular layer of said first solid particles;

(g) blending a second mixture comprising

- (i) finely divided second solid particles having a chemical composition which is different from said chemical composition of said first solid particles,
- (ii) a second binder operable upon curing for bonding said finely divided second solid particles together, and
- (iii) a second solvent for said second binder, into an uniformly dispersed second slurry, said second binder and said second solvent not being capable

of chemically attacking said first binder in said thusly produced outer, densely packed, bonded, annular layer of said first solid particles;

(h) rotating said internal molding surface containing said outer, densely packed, bonded, annular layer of said first solid particles;

(i) introducing said thusly blended uniformly dispersed second slurry onto said rotating outer, densely packed, bonded, annular layer of said first solid particles;

(j) applying an effective centrifugal force to said second slurry thusly introduced onto said rotating outer, densely packed, bonded, annular layer of said first solid particles which is operable for transforming said second slurry into a second, densely packed, annular layer of said second solid particles coated with a small amount of said second solvent and said second binder which is compressed against said outer, densely packed, bonded, annular layer of said first solid particles by said last mentioned centrifugal force, and an inner annular layer of said second solvent and said second binder which is compressed against said second, densely packed, annular layer of said second solid particles by said last mentioned centrifugal force, the amount of said second binder used for forming said uniformly dispersed second slurry in step (g) being in excess of an amount required to bond said second solid particles together;

(k) after forming said second, densely packed, annular layer of said second solid particles and said inner annular layer of said second solvent and said second binder, removing said second solvent therefrom by evaporation;

(l) allowing said second binder coating said second solid particles in said second, densely packed, annular layer of said second solid particles to bond said second solid particles thereof together thereby forming a second, densely packed, bonded, annular layer of said second solid particles, and allowing said second binder in said last mentioned inner annular layer to cure into a solid state thereby forming an inner annular layer of cured second binder;

(m) removing said last mentioned applied centrifugal force from said annular layers and thereafter separating said inner annular layer of cured second binder from said second, densely packed, bonded, annular layer of said second solid particles;

(n) blending a thirs mixture comprising

(i) finely divided third solid particles having a chemical composition which is different from said chemical composition of said second solid particles;

(ii) a third binder operable for bonding said finely divided third solid particles together, and

(iii) a third solvent for said third binder, into an uniformly dispersed third slurry, said third binder and said third solvent not being capable of chemically attacking said second binder in said thusly formed second, densely packed, bonded, annular layer of said second solid particles;

(o) rotating said internal molding surface containing said outer, densely packed, bonded annular layer of said first solid particles and said second, densely packed, bonded, annular layer of said second solid particles;

(p) introducing said thusly blended uniformly dispersed third slurry onto said rotating second, densely packed, bonded, annular layer of said second solid particles;

(q) applying an effective centrifugal force to said second slurry thusly introduced onto said rotating seocnd, densely packed, bonded, annular layer of said second solid particles which is operable for transforming said third slurry into a third, densely packed, annular layer of said third solid particles coated with a small amount of said third solvent and said third binder which is compressed against said second, densely packed, bonded, annular layer of said second solid particles by said last mentioned centrifugal force, and an inner annular layer of said third solvent and said third binder which is compressed against said third, densely packed, annular layer of said third solid particles by said last mentioned centrifugal force, the amount of said third binder used for forming said uniformly dispersed third slurry in step (n) being in excess of an amount required to bond said third solid particles together;

(r) after forming said third, densely packed, annular layer of said third solid particles and said inner annular layer of said third solvent and said third binder, removing said third solvent threfrom by evaporation;

(s) allowing said third binder coating said third solid particles in said third, densely packed, annular layer of said third solid particles to bond said third solid particles thereof together thereby forming a third, densely packed, bonded, annular layer of said third solid particles, and allowing said third binder in said last mentioned inner annular layer to cure into a solid state thereby forming an inner annular layer of cured third binder;

(t) removing said last mentioned applied centrifugal force from said annular layers and thereafter separating said inner annular layer of cured third binder from said third, densely packed, bonded, annular layer of said third solid particles thereby forming a composite layer structure which comprises said outer, densely packed, bonded, annular layer, of said first solid particles which is bonded to said second, densely packed, bonded, annular layer of said second solid particles, which is bonded to said third, densely packed, bonded, annular layer of said third solid particles; and

(u) separating said composite layer structure from said internal molding surface thereby producing a multilayer tape of densely packed, bonded solid particles.

17. The method of calim 16, wherein said chemical compsoption of said finely divided first and third solid particles is strontium lanthenum manganite, and said chemical composition of said finely divided second solid particles is yttria stabilized zirconia.

18. The method of calim 17, wherein said first and third binder is polyvinyl butyral, said second binder is linseed oil, said first and third solvent is methylene chloride, and said second solvent is petroleum spirits.

19. A method of producing a multilayer tape of sensely packed, bonded solid particles comprising a layer of yttria stabilized zirconia particles sandwiched between and bonded to layers of filament shaped fragments of bonded agglomerates of strontium lanthanum manganite particles comprising:

(a) blending a mixture comprising

- (i) finely divided solid particles of strontium lanthanum manganite,
- (ii) a binder operable for bonding said solid particles together, and
- (iii) a solvent for said binder, into an uniformly dispersed slurry;
- (b) transforming said slurry into a plurality of downwardly falling filaments;
- (c) deflecting and drying said plurality of downwardly falling filaments with a plurality of impinging gas streams operative for deflecting and bending said filaments into a plurality of downwardly falling sinuous filaments while simultaneously removing said solvent therefrom by evaporation;
- (d) collecting said plurality of sinuous filaments on a moving surface in such a manner that said plurality of sinuous filaments overlap each other in a predetermined amount thereby forming a mat of overlying sinuous filaments having a predetermined thickness;
- (e) compressing said mat to increase the filament-to-filament contact therein thereby producing a pressed mat;
- (f) sintering said pressed mat at a temperature operable for increasing the amount of filament-to-filament bonding therein thereby providing a bonded mat;
- (g) comminuting said bonded mat thereby producing filament shaped fragments of bonded agglomerates of strontium lanthanum manganite particles;
- (h) blending a first mixture comprising
  - (i) said filament shaped fragments produced in step (g),
  - (ii) a first binder operable upon curing for bonding said filament shaped fragments together, and
  - (iii) a first solvent for said first binder, into an uniformly dispersed first slurry;
- (i) introducing said thusly blended uniformly dispersed first slurry onto a rotating internal molding surface;
- (j) applying an effective centrifugal force to said first slurry thusly introduced onto said rotating internal molding surface which is operable for transforming said first slurry into an outer, densely packed, annular layer of said filament shaped fragments coated with a small amount of said first solvent and said first binder which is compressed against said molding surface by said centrifugal force, and an inner annular layer of said first solvent and said first binder which is compressed against said outer, densely packed, annular layer of said filament shaped fragments by said centrifugal force, the amount of said first binder used for forming said uniformly dispersed first slurry in step (h) being in excess of an amount required to bond said filament shaped fragments together;
- (k) after forming said outer and inner layers and while applying said centrifugal force, removing said first solvent from said outer and inner annular layers by evaporation;
- (l) allowing said first binder coating said filament shaped fragments in said outer, densely packed, annular layer to bond said filament shaped fragments together thereby forming an outer densely packed, bonded, annular layer of said filament shaped fragments, and allowing said first binder in said inner annular layer to cure into a solid state

- thereby forming an inner annular layer of cured first binder;
- (m) removing said applied centrifugal force from said outer and inner annular layers and thereafter separating said inner annular layer of cured first binder from said outer, densely packed, bonded annular layer of said filament shaped fragments;
- (n) blending a second mixture comprising
  - (i) finely divided yttria stabilized zirconia particles,
  - (ii) a second binder operable upon curing for bonding said finely divided yttria stabilized zirconia particles together, and
  - (iii) a second solvent for said second binder, into an uniformly dispersed second slurry, said second binder and said second solvent not being capable of chemically attacking said first binder in said thusly produced outer, densely packed, bonded, annular layer of said filament shaped fragments;
- (o) rotating said internal molding surface containing said outer, densely packed, bonded, annular layer of said filament shaped fragments;
- (p) introducing said thusly blended uniformly dispersed second slurry onto said rotating outer, densely packed, bonded, annular layer of said filament shaped fragments;
- (q) applying an effective centrifugal force to said second slurry thusly introduced onto said rotating outer, densely packed, bonded, annular layer of said filament shaped fragments which is operable for transforming said second slurry into a second, densely packed, annular layer of said yttria stabilized zirconia particles coated with a small amount of said second solvent and said second binder which is compressed against said outer, densely packed, bonded, annular layer of said filament shaped fragments by said last mentioned centrifugal force, and an inner annular layer of said second solvent and said second binder which is compressed against said second, densely packed, annular layer of said yttria stabilized zirconia particles by said last mentioned centrifugal force, the amount of said second binder used for forming said uniformly dispersed second slurry in step (n) being in excess of an amount required to bond said yttria stabilized zirconia particles together;
- (r) after forming said second, densely packed, annular layer of said yttria stabilized zirconia particles and said inner annular layer of said second solvent and said second binder, removing said second solvent therefrom by evaporation;
- (s) allowing said second binder coating said yttria stabilized zirconia particles in said second, densely packed, annular layer of said yttria stabilized zirconia particles to bond said yttria stabilized zirconia particles thereof together thereby forming a second, densely packed, bonded, annular layer of said yttria stabilized zirconia particles, and allowing said second binder in said last mentioned inner annular layer to cure into a solid state thereby forming an inner annular layer of cured second binder;
- (t) removing said last mentioned applied centrifugal force from said annular layers and thereafter separating said inner annular layer of cured second binder from said second, densely packed, bonded, annular layer of said yttria stabilized zirconia particles;
- (u) blending a third mixture comprising

- (i) said filament shaped fragments produced in step (g),
- (ii) a third binder operable for bonding said filament shaped fragments together, and
- (iii) a third solvent for said third binder, into an 5 uniformly dispersed third slurry, said third binder and said third solvent not being capable of chemically attacking said second binder in said thusly formed second, densely packed, bonded, annular layer of said yttria stabilized zirconia particles;
- (v) rotating said internal molding surface containing said outer, densely packed, bonded annular layer of said filament shaped fragments and said second, densely packed, bonded, annular layer of said yttria 15 stabilized zirconia particles;
- (w) introducing said thusly blended uniformly dispersed third slurry onto said rotating second, densely packed, bonded, annular layer of said yttria stabilized zirconia particles;
- (x) applying an effective centrifugal force to said second slurry thusly introduced onto said rotating second, densely packed, bonded, annular layer of said yttria stabilized zirconia particles which is operable for transforming said third slurry into a 20 third, densely packed, annular layer of said filament shaped fragments coated with a small amount of said third solvent and said third binder which is compressed against said second, densely packed, bonded, annular layer of said yttria stabilized zirconia particles by said last mentioned centrifugal force, and an inner annular layer of said third solvent and said third binder which is compressed against said third, densely packed, annular layer of 25 said filament shaped fragments by said last mentioned centrifugal force, the amount of said third binder used for forming said uniformly dispersed third slurry in step (u) being in excess of an amount required to bond said filament shaped fragments together;
- (y) after forming said third, densely packed, annular layer of said filament shaped fragments and said inner annular layer of said third solvent and said third binder, removing said third solvent therefrom by evaporation;
- (z) allowing said third binder coating said filament shaped fragments in said third, densely packed, f annular layer of said filament shaped fragments to bond said filament shaped fragments thereof together thereby forming a third, densely packed, bonded, annular layer of said filament shaped fragments, and allowing said third binder in said last mentioned inner annular layer to cure into a solid state thereby forming an inner annular layer of 30 cured third binder;
- (aa) removing said last mentioned applied centrifugal force from said annular layers and thereafter separating said inner annular layer of cured third binder from said third, densely packed, bonded, annular layer of said filament shaped fragments thereby 35 forming a composite layer structure which comprises said outer, densely packed, bonded, annular layer, of said filament shaped fragments which is bonded to said second, densely packed, bonded, annular layer of said yttria stabilized zirconia particles, which is bonded to said third, densely packed, bonded, annular layer of said filament shaped fragments; and

- (bb) separating said composite layer structure from said internal molding surface thereby producing a multilayer tape of densely packed, bonded solid particles comprising a layer of yttria stabilized zirconia particles sandwiched between and bonded to layers of filament shaped fragments of bonded agglomerates of strontium lanthanum manganite particles.
- 20. A method of forming a mat of overlying sinuous ceramics filaments having a predetermined thickness comprising:
  - (a) blending a mixture comprising
    - (i) finely divided solid ceramic particles,
    - (ii) a binder operable for bonding said solid ceramic particles together, and
    - (iii) a solvent for said binder, into an uniformly dispersed slurry;
  - (b) extruding said slurry into a plurality of downwardly falling filaments having a width of at least about 0.00025 inches;
  - (c) deflecting said plurality of downwardly falling filaments with a plurality of impinging gas streams operative for deflecting and bending said filaments into a plurality of downwardly falling sinuous filaments while simultaneously removing said solvent therefrom by evaporation; and
  - (d) collecting said plurality of sinuous filaments on a moving surface in such a manner that said plurality of sinuous filaments overlap each other a predetermined amount thereby forming a mat of overlying sinuous filaments having a predetermined thickness.
- 21. A method of producing filament shaped fragments of bonded agglomerates of strontium lanthanum manganite particles comprising:
  - (a) blending a mixture comprising
    - (i) finely divided solid particles of strontium lanthanum manganite,
    - (ii) a binder operable for bonding said solid particles together, and
    - (iii) a solvent for said binder, into an uniformly dispersed slurry;
  - (b) extruding said slurry into a plurality of downwardly falling filaments;
  - (c) deflecting and drying said plurality of downwardly falling filaments with a plurality of impinging gas streams operative for deflecting and bending said filaments into a plurality of downwardly falling sinuous filaments while simultaneously removing said solvent therefrom by evaporation;
  - (d) collecting said plurality of sinuous filaments on a moving surface in such a manner that said plurality of sinuous filaments overlap each other a predetermined amount thereby forming a mat of overlying sinuous filaments having a predetermined thickness;
  - (e) compressing said mat to increase the filament-to-filament contact therein thereby producing a pressed mat;
  - (f) sintering said pressed mat at a temperature operable for increasing the amount of filament-to-filament bonding therein thereby providing a bonded mat; and
  - (g) comminuting said bonded mat thereby producing filament shaped fragments of bonded agglomerates of strontium lanthanum manganite particles, wherein said thusly produced fragments have a length of at least about 0.003 inches and a width of at least about 0.00025 inches.

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